THE INTRAMOLECULAR DYNAMICS OF A 'RIGID YET TWISTY' FERROCENYL TETRAPHOSPHINE – SERVED WITH SOME ^{31}P-NMR DELICACY

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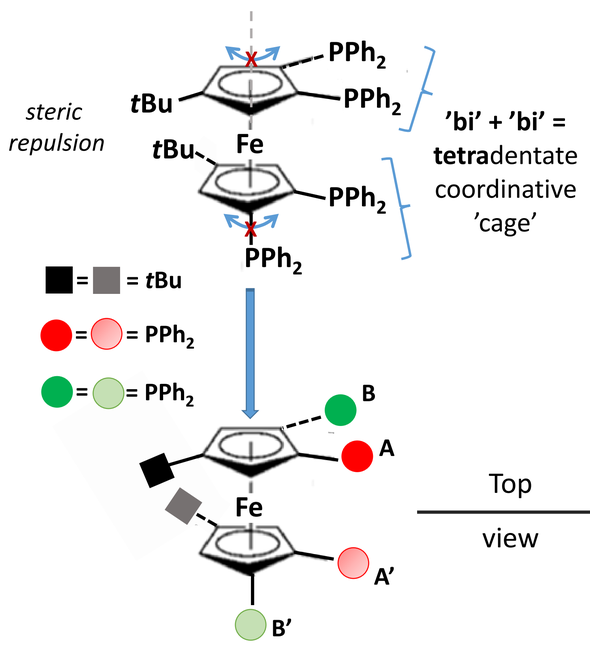
Introduction: multidentate ferrocenyl phosphines

- Multidentate ferrocenyl phosphines offers multiple coordinative sites for a ≡P**:** lone electron pair acceptor
- The Cp rings are typically equipped with bulky substituents → the antiparallel ring rotation (twisting) is hindered → a permanent coordinative 'cage' is formed consisted of multiple coordinative sites
- Application: molecular cluster, nanoparticle, surface stabilizators/activators [1], and common ligands in transition metal catalyzed Suzuki cross-coupling reactions [2]

Investigated molecule: Fc(P)$_4$*t*Bu



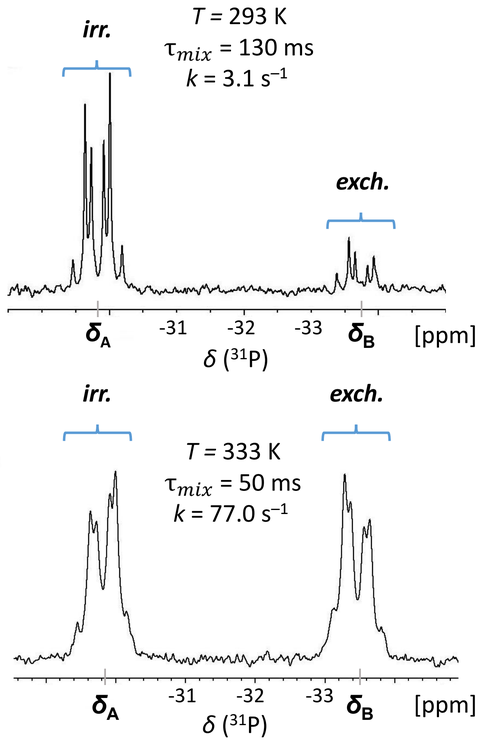
Objectives: hindered motions to reveal

- Conception of 'static, rigid' conformation (see left) to be refined
- Hindered antiparallel Cp rotations to characterize – both in a qualitative and quantitative fashion
- Sufficiently long time scale is needed ... →

NMR spectroscopy!

Results: and yet it moves!

1D ^{31}P-{^{1}H} sEXSY
T = 293 K
τ_{mix} = 130 ms
k = 3.1 s^{-1}

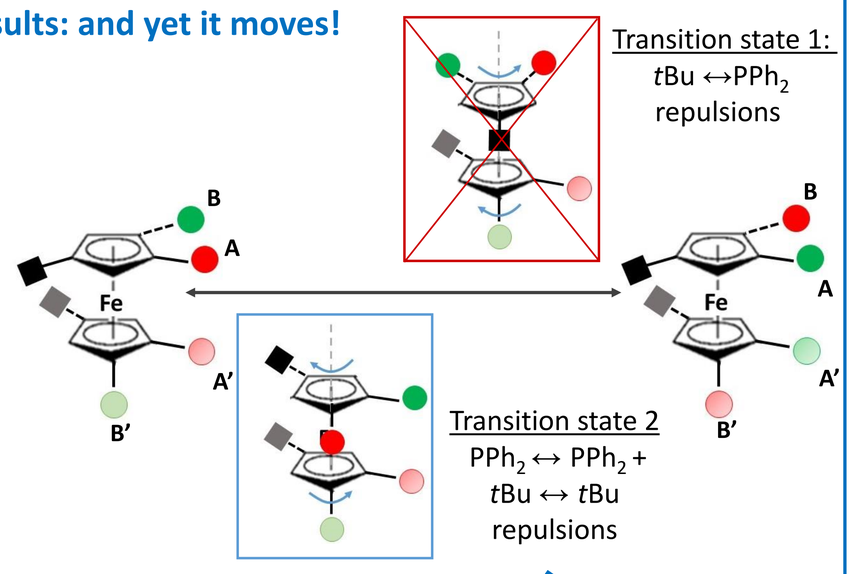


solvent: toluene-d8

- Elevation of *T* → line broadenings
- 1D selective ^{31}P EXSY experiments

→ A(A') ↔ B(B') dynamic exchange

→ **Relative twisting of the rings**



- From $k_{rot}(T)$ → $\Delta H^{\#}_{rot}$ and $\Delta S^{\#}_{rot}$ (via Eyring-plot [3])

→ $\Delta G^{\#}_{rot,298\,K}$ (exp.) = 69.0 kcal·mol^{-1}

- According to DFT calculations (PBE1PBE/Def2SVP-w06)

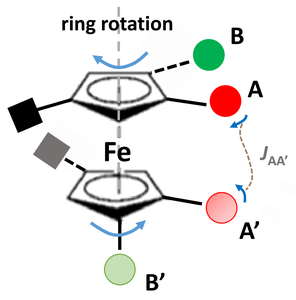
$\Delta G^{\#}_{298\,K}$ (theor.) = 68.9 kcal·mol^{-1} for transition state 2

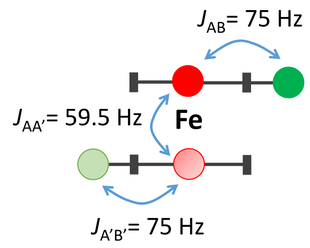
→ **Preferred way of (hindered) rotation keeps the coordinative sites close**

J$_{AA'}$: *through space* or not?

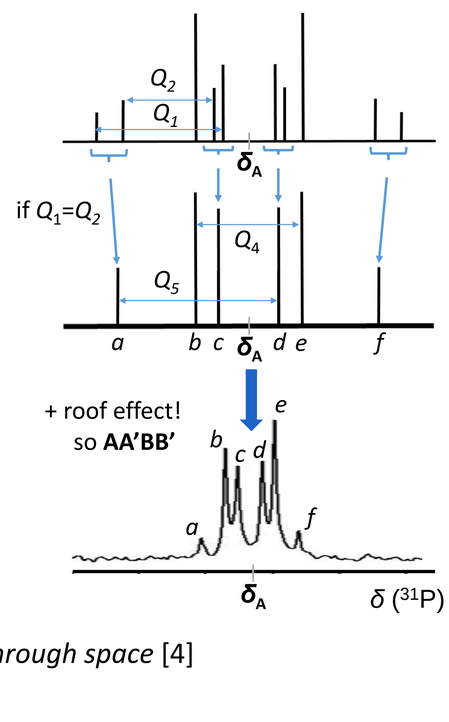
k_{rot}(333 K)= 77.0 ± 0.2 Hz > 59.5 Hz = $J_{AA'}$

and still AA'BB' !

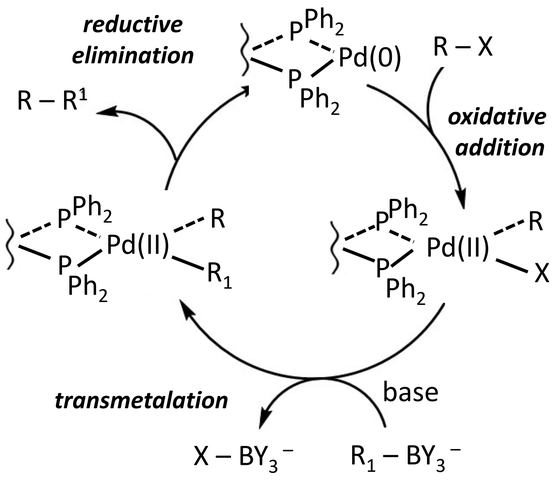




- $^3J_{AA'}$ is reported to be *through space* [4]



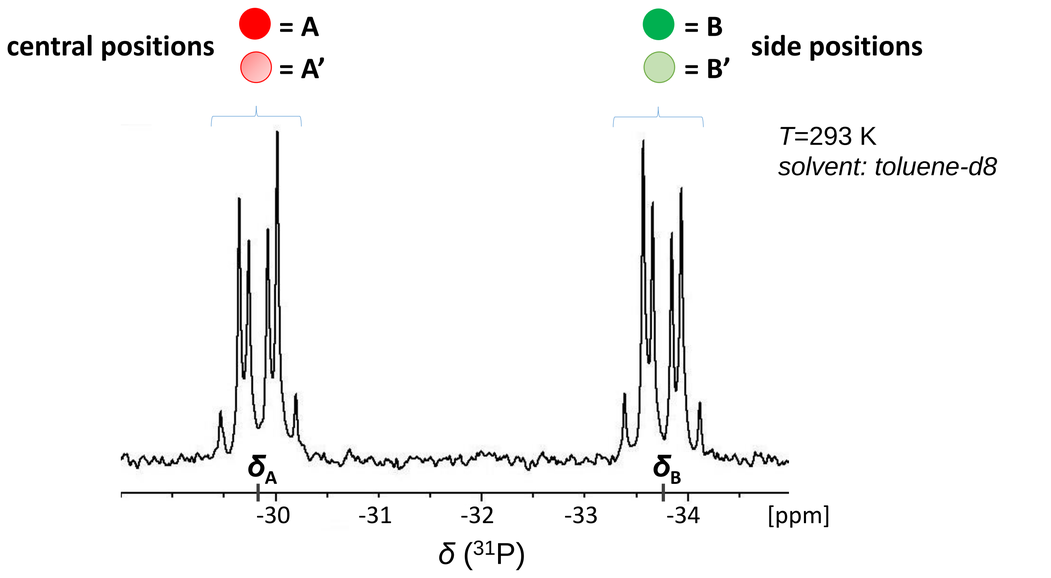
Reminder on Suzuki cross-couplings



- Metal center is solubilized before *oxidative addition* by the phosphine
- Bulkiness of the ligand facilitates the *reductive elimination* step
- Multiple coordinative sites provide longer catalytic lifetime and higher efficiency

^{31}P-{^{1}H} NMR spectrum of Fc(P)$_4$*t*Bu*

- 2 chemical environments (red and green) for the 4 phosphorus nuclei due to symmetry



- Both peaks in the ^{31}P-{^{1}H} display puzzling patterns → couplings between ^{31}P-s on different Cp rings exist → 4-membered spin system (but A_2X_2, A_2B_2, AA'XX', or AA'BB' ?)

→ **AA'XX'** spin system with subtle second order effects! Centrosymmetric spectrum

- In principle, for each spin 10–10 (spin-allowed) transition frequencies are conceivable if $J_{AA'} \neq J_{XX'} \neq J_{AX'}=J_{A'X} \neq J_{AX}=J_{A'X'} \neq 0$
- How to read the scalar coupling constant values?

$Q_1 : Q_3 : Q_5 =$
$(2C^2 - 1) : (2C\sqrt{1-C^2}) : 1$
→ Q_3=75 Hz=Q_4

$J_{AX'}=J_{A'X}=\frac{1}{2}(Q_4-Q_3)=0$ Hz
$J_{AA'}=\frac{1}{2}(Q_1+Q_2)=59.5$ Hz
$J_{AX}=J_{A'X'}=\frac{1}{2}(Q_3+Q_4)=75$ Hz
$J_{XX'}=\frac{1}{2}(Q_1-Q_2)=0$ Hz

At δ_A for instance:

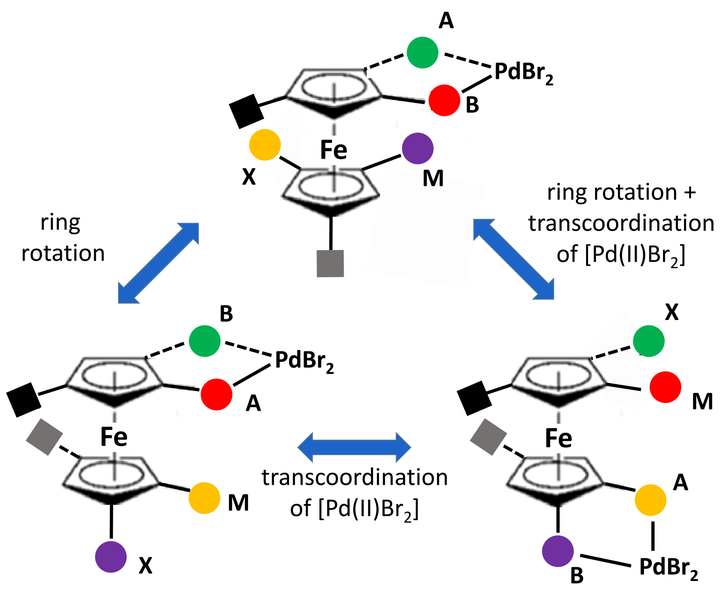
Results II – [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu]

- [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu]: 16 e$^-$ state of Pd
- ABMX ^{31}P spin system (4 peaks)
- 1D ^{31}P and 2D ^{1}H EXSY-s

→ A ↔ B ↔ M ↔ X are in dynamic exchange

→ **Ring rotation + transcoordination of =PdBr$_2$**

- Benefits of multiple coordinative sites
- *k*(rot) > *k*(transc.)



Conclusions

- The 'rigidity' of the Cp scaffold in Fc(P)$_4$*t*Bu was quantified experimentally and *in silico*
- The preferred pathway of the hindered Cp ring twisting supports the existence of a permanent multidentate coordinative 'cage'
- Transition metal transcoordination between distinct coordinative sites was directly shown in case of [Pd(II)Br$_2$-Fc(P)$_4$*t*Bu]

Acknowledgements

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References

[1] Zhang, S., Leem, G. *et. al., J. Am. Chem. Soc.,* 2008, **130**, 113-120 [2] Hierso, J-C., Fihri, A. *et. al., Organometallics,* 2003, **22,** 4490-4499 [3] Bain, A., Chemical Exchange in NMR, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2003, **43**, 63-103 [4] Hierso, J-C., Fihri, A., Ivanov, V. V., Hanquet, B., Pirio, N., *et. al., J. Am. Chem. Soc.,* 2004, **126**, 11077-11087

*Note: the assignments of the ^{31}P NMR spectra were adapted from [4]. However, the interpretation of the peak multiplicities and the investigation of dynamic properties are novel results and the product of the authors of this work.

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